I. THE STRUCTURE OF THE SELF-CONDENSATION PRODUCT OF 1-PHENYL-2-PYRAZOLINE

II. REACTIONS OF ACETOPHENONE IN THE PRESENCE OF POLYPHOSPHORIC ACID

BY

DAVID BRUCE BRIGHT

B. C., University of Minnesota, 1949
M. S., University of Illinois, 1950

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS
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I. THE STRUCTURE OF THE SELF-CONDENSATION PRODUCT OF 1-PHENYL-2-PYRAZOLINE

Introduction

In the course of an investigation of the behavior of 1-aryl-2-pyrazolines (cyclic phenylhydrazones) toward acid reagents,[1] it was found that 1-phenyl-2-pyrazoline formed a self-condensation product in the presence of boron fluoride, ferric chloride, or hydrogen chloride. It was established that the product was a bi-2-pyrazoline with the 3-position of one of the pyrazoline units as a point of union. A synthesis of 1,1′-diphenyl-3,4′-bipyrazole was proposed for the purpose of comparing the product with a bipyrazole obtained by the oxidation of the self-condensation product.

The object of the present research was to complete the proposed synthesis of 1,1′-diphenyl 3,4′-bipyrazole and to establish the structure of the self-condensation product.

Discussion Of Results

The proposed synthesis of 1,1′-diphenyl-3,4′-bipyrazole was completed, and this compound was shown to be different from the bipyrazole derived from the self-condensation product of 1-phenyl-2-pyrazoline. The synthesis involved the characterization of the intermediate products, methyl 3-(5-methyl-1-phenylpyrazolyl)-acetate, 1-phenyl-4-(1-phenyl-5-methyl-3-pyrazolyl)-5-pyrazolone, 1,1′-diphenyl-5-methyl-3,4′-bipyrazole, and 1,1′ diphenyl-3,4′ bipyrazole-5-carboxylic acid.

The bipyrazole produced by the oxidation of the self condensation product was shown to be identical with 1,1′ diphenyl 3,3′-bipyrazole, which was prepared by an unequivoval method. The intermediate products of the synthesis, diethyl 5-methyl-1-phenylpyrazole-3-carbonylmalonate, 1 phenyl 3-(5 methyl-1-phenyl-3-pyrazolyl)-5-pyrazolone, 1,1′-diphenyl-5-methyl-5′-bromo-3,3′-bipyrazole, 1,1′-diphenyl-5-methyl 3,3′-bipyrazole, and 1,1′-diphenyl 3,3′-bipyrazole-5-carboxylic acid, have been characterized.

With the identification of its bipyrazole derivative, the self-condensation product of 1-phenyl 2 pyrazoline is shown to be 1,1′-diphenyl-3,3′-bi 2 pyrazoline, and the proof of structure is complete.

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II. REACTIONS OF ACETOPHENONE IN THE PRESENCE OF POLYPHOSPHORIC ACID

Introduction

It has recently been established[1] that in the presence of polyphosphoric acid certain carbonyl compounds condense with active aromatic nuclei to form 1,1-diarylalkenes or 1,1,1-triarylalkanes. However, when the reaction was applied to acetophenone and benzene, the expected products, 1,1-diphenylethylene and 1,1,1-triphenylethane, were not obtained. Instead, a yellow crystalline hydrocarbon was formed. The empirical formula, $C_{32}H_{24}$, was demonstrated by analyses and molecular weight determinations, and a tetrahydro derivative was obtained by catalytic hydrogenation.

In the course of an earlier investigation, Delacre[2] obtained from derivatives of acetophenone several hydrocarbons having the empirical formula, $C_{32}H_{24}$, the structures of which were not ascertained.

In the present work the reaction of acetophenone with benzene in the presence of polyphosphoric acid was reinvestigated for the purpose of gaining more information about the formation and structure of the yellow hydrocarbon. It was also proposed to determine the nature of the relationship, if any, between the yellow hydrocarbon and the hydrocarbons obtained by Delacre.

Discussion Of Results

From the reaction of acetophenone in the presence of benzene and polyphosphoric acid, five products were isolated: benzoic acid, dypnone, the $C_{32}H_{24}$ hydrocarbon (I) described by Roeske[1], a higher melting hydrocarbon (II), and a yellow substance (III) that melts above 300°. It was shown that dypnone is a probable intermediate in the formation of I, II, and III. Benzene functions only as a solvent in the process.

The reaction of I with butyllithium followed by carbonation gives an acid having the empirical formula, $C_{37}H_{34}O_2$. The corresponding methyl ester is also prepared. The reaction of I with lithium aluminum hydride gives a dihydro derivative. With maleic anhydride I yields a mono adduct and, at a higher temperature, a tetra adduct. Nitrous acid reacts with I to form an unidentified white product which is converted by heat into an orange nitro derivative, $C_{32}H_{23}NO_2$ Benzoic acid is obtained by the oxidation of I with dilute nitric acid.

"Dypnopinacol" (2,4,6 triphenyl-2-hydroxy-6 methyl-1,2,5,6-tetrahydrobenzophenone) reacts in the presence of polyphosphoric acid to give III in quantitative yield. The precursors, "*a* dypnopinacolone" (2,4,6 triphenyl-2 methyl-2,3 dihydrobenzophenone) and "*a* isodypnopinacolone" (2,4,6 triphenyl-4-methyl 3,4-dihydrobenzophenone), of two $C_{32}H_{24}$ hydrocarbons obtained by Delacre are not intermediates in the formation of I or II; and these hydrocarbons of Delacre bear no apparent relationship to I and II other than the fact that the four compounds are all derived from dypnone.

A structure (1,3,9 triphenyl-4a methyl 4a-isofluorene) consistent with the chemical behavior and the infrared and ultraviolet spectra of I and its derivativies is suggested for the yellow hydrocarbon (I). A logical sequence of reactions leading to the formation of the structure is also suggested.

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VITA

David Bruce Bright was born on August 5, 1927, in Great Falls, Montana. After graduating from Great Falls High School in 1945, he entered the University of Minnesota and received the degree of Bachelor of Chemistry, with distinction, in June, 1949. In September of that year he entered the Graduate College of the University of Illinois and received the Master of Science degree in August, 1950. He served as a teaching assistant from September, 1949, until August, 1951, and held an Atomic Energy Commission Fellowship in the academic year 1951-52.